

# Accurate prediction of the glass transition in classical fluids: a pragmatic modification of the mode coupling theory

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## Abstract

Many qualitative observations on the glass transition in classical fluids are well described by the mode coupling theory (MCT) but the extent of the non-ergodicity domain is often over-estimated by this theory. Making it more quantitative while preserving its microscopic nature remains thus a current challenge. We propose here a simple heuristic modification that achieves this for the long-time limit quantities by reducing the excess of static correlations that are presumably responsible for its inaccuracy. The location of the ideal glass transition predicted from this modified MCT compares very well with simulation for a wide range of interaction potentials in pure fluids and in mixtures.

Being based on a time evolution equation deduced from a true hamiltonian, MCT is one of the few microscopic theories of the glass transition [1]. Developed initially for atomic fluids, its has more recently regained interest for describing the ideal glass transition in soft condensed matter [2, 3]. While it reproduces important qualitative observations in both physical situations, it suffers from quantitative limitations due to its approximate treatment of the time evolution equation. Examples are the critical packing fraction  $\eta_g^{MCT} = 0.525$  of the hard-sphere (HS) glass instead of  $\eta_g^{ex} \approx 0.58$  from experiments on HS colloids [4], the critical temperature  $T_g^{MCT}$  for the Lennard-Jones (LJ) fluid being in error by a factor two [5] and the whole  $T_g^{MCT}(\rho)$  curve for the square-well (SW) fluid [6] clearly misplaced in the temperature-density plane. Some ad-hoc recipes have been proposed to

correct this in specific situations such as the LJ mixture [7], but they are not completely satisfactory. Comparison with experiment or simulation is usually done by rescaling the state variables (see for example [6]), but at the expense of the microscopic nature of the theory [8, 9]. To go beyond this, one should start from the basic approximations of MCT. Besides the projection of the dynamical variables on specific subsets, an important one is the factorization of four point contributions as products of pair terms[1, 2]. The static structure appears then in MCT at the level of the structure factors  $S_{\alpha\beta}(q)$  and the triplet direct correlation functions (dcfs)  $c_{\alpha\beta}^{(3)}(q)$  (in Fourier space). The latter can usually be neglected (convolution approximation), as shown by previous estimates [10] and confirmed by more recent ones [11]. As the liquid-glass transition is not very sensitive to the quality of the static structure, at least for hard-spheres [12], it is tempting to view this overestimation by MCT of the non-ergodicity domain as reflecting too strong pair correlations, and attribute this to the factorization approximation. They should accordingly be reduced (the possibility to predict the dynamics only from the static structure has recently been criticized [8]. However, the factored four point terms involving two time-dependent densities in  $\mathbf{q}$  space, it is understandable that this approximation is more critical for the time dependence since different time scales might be improperly mixed). In this letter, we propose and test a pragmatic way of implementing this idea in the long-time limit: to reduce correlations, one should compute the static structure at an effective density that is lower (or a temperature higher) than the actual one (see [7] for a similar attempt). To see how this can be done in practice, recall that the densities  $\rho_\alpha = \frac{N_\alpha}{V}$  enter the MCT time evolution of the matrix  $\mathbf{S}(q; t)$  with elements  $S_{\alpha\beta}(q; t)$

$$\frac{\partial}{\partial t}\mathbf{S}(q; t) + q^2\mathbf{H}(q)\mathbf{S}^{-1}(q)\mathbf{S}(q; t) + \int_0^t dt'\mathbf{M}(q; t - t')\mathbf{H}^{-1}(q)\frac{\partial}{\partial t'}\mathbf{S}(q; t') = 0 \quad (1)$$

through the irreducible collective memory function whose matrix elements are [13, 14]:

$$M_{\mu\nu}(q, t) = \frac{D_\mu^0 D_\nu^0}{16\pi^3(\rho_\mu \rho_\nu)^{(1/2)}} \sum_{\gamma\gamma'\delta\delta'} \int d\mathbf{k} V_{\mu;\gamma\delta}(\mathbf{q}, \mathbf{k}) V_{\nu;\gamma'\delta'}(\mathbf{q}, \mathbf{k}) S_{\gamma\gamma'}(\|\mathbf{q}-\mathbf{k}\|; t) S_{\delta\delta'}(k; t) \quad (2)$$

In the vertex amplitude,

$$V_{\mu;\gamma\delta}(\mathbf{q}, \mathbf{k}) = \frac{1}{q} [\mathbf{q} \cdot \mathbf{k} \delta_{\mu\delta} C_{\mu\gamma}(k) + \mathbf{q} \cdot (\mathbf{q} - \mathbf{k}) \delta_{\mu\gamma} C_{\mu\delta}(\|\mathbf{q} - \mathbf{k}\|) + q^2 x_\mu^{1/2} C_{\mu\gamma\delta}^{(3)}(\mathbf{k}, \mathbf{q} - \mathbf{k})] \quad (3)$$

the static dcfs are computed from standard methods of liquid state theory with the actual densities  $\rho_\alpha$  as input. The modification consists then in using effective densities  $\rho_\alpha^{eff}$  (specified below) in the vertex while retaining in  $M_{\mu\nu}$  the explicit dependence on density in the factor before the integral. As a result, the MCT equation is solved for the actual densities but with a static structure computed for  $\rho_\alpha^{eff}$ . Similarly, an effective temperature

$T^{eff}$  is used when temperature is a relevant variable. It is stressed that this is not a mere rescaling of the variables, a posteriori. Rather, this amounts to solving a modified MCT equation with an "effective" pair structure. To distinguish the results relative to the original MCT from those obtained from the modified MCT, we shall label the latter by a tilde (the label ex will refer to experiment, mostly computer ones here).

To calibrate the correction, we start from the hard sphere potential for which there is a purely repulsive glass (caging mechanism). From the difference  $\Delta\eta = 0.055$  between the experimental critical glass packing fraction  $\eta_g^{ex} = 0.58$  and the MCT one  $\eta_g^{MCT} = 0.525$  with accurate static input [5, 11], we solve the MCT equation for the non-ergodicity parameter  $f(q)$  - at the packing fraction  $\eta$  - by using the structure factor  $S(q; \eta^{eff})$  for an effective packing fraction  $\eta^{eff} = \eta - 0.055$ . The solution of this modified integral equation is the standard method of direct iterations [1]. The first non trivial result is that these iterations converge to a new critical value  $\tilde{\eta}_g^{MCT} = 0.584$ , virtually the exact one (ie  $\eta_g^{MCT} + \Delta\eta$ ). Equipped with this calibration, we consider a binary hard-sphere mixture (size ratio  $\delta = D_1/D_2$ , packing fractions  $\eta_1$  and  $\eta_2$ ). The effective packing fractions are then  $\eta_i^{eff} = \eta_i - \Delta\eta(1 - \eta_j/\eta_g^{ex})$ ;  $i \neq j = 1, 2$ . The slight dependence on the packing fraction of the other species is introduced so as to recover the one-component correction and prevent negative value. As with the one component case, we found that the modified MCT equations converge nearly to the corrected density, up to a size ratio  $\delta = 0.1$ . Quantitatively, the correction was tested on two HS mixtures considered in ref. [15]. For  $\delta = 0.6$  and  $\hat{x} = \eta_1/\eta = 0.2$ , the total critical packing fractions are  $\eta_g^{MCT} = 0.528$ ,  $\tilde{\eta}_g^{MCT} = 0.593$ , while  $\eta_g^{ex} = 0.606$  from simulation. For  $\delta = 0.83$  and  $\hat{x} = 0.37$ ,  $\eta_g^{MCT} = 0.524$ ,  $\tilde{\eta}_g^{MCT} = 0.589$  and  $\eta_g^{ex} = 0.586$ . For both mixtures, the values predicted by the modified MCT are thus very close to simulation. This definitive improvement is confirmed by figure 1, which shows, as an example, the non ergodicity parameter  $f_{11}(q)$  for  $\delta = 0.6$ . This excellent agreement with simulation - at the new critical density- is consistent with the relation  $\eta_g^{eff} \approx \eta_g^{ex} - \Delta\eta$ . It reflects the fact that the original MCT predicts the correct critical non-ergodicity parameter but a slightly inaccurate critical density, as found in [12].

To go beyond the HS model, we first took the soft sphere potential  $\phi = \epsilon(\frac{\sigma}{r})^{12}$  for which density and temperature are combined in the coupling constant  $\Gamma = \rho\sigma^3(\epsilon/k_B T)^{1/4}$ . The one-component fluid of soft spheres has a critical coupling constant  $\Gamma_g^{ex} = 1.5$  (see [16]). Using the Rogers-Young closure for the static structure as in ref. [17], one gets  $\Gamma_g^{MCT} = 1.33$ . Using as the only information the one gained from the HS potential, we compute the static structure in the modified MCT with an effective coupling constant  $\tilde{\Gamma} = \Gamma - 1.33(0.58/0.525 - 1)$ . We then find a new critical coupling constant  $\tilde{\Gamma}_g^{MCT} = 1.51$  again in very good agreement with simulation. We next took the mixture considered by

Barrat and Latz. One finds  $\Gamma_g^{MCT} = 1.32$  significantly lower than the simulation value  $\Gamma_g^{MCT} = 1.46$  ( $\sigma^3$  is replaced by  $\sigma_{eff}^3 = x_1^2\sigma_{11}^3 + 2x_1x_2\sigma_{12}^3 + x_2^2\sigma_{22}^3$  in the definition of  $\Gamma$ ). With the modified MCT, the improvement is clear:  $\tilde{\Gamma}_g^{MCT} = 1.51$ . (using .575 instead of .58, we get  $\tilde{\Gamma}_g^{MCT} = 1.48$  virtually the exact result).

To consider a model with attractive contributions, we took the LJ fluid for which simulation data have been collected in [5] and more recently in [18]. Temperature plays now a role (the reduced temperature  $T^* = k_B T / \epsilon$  is used): a large error in the critical temperature  $T_g^{MCT}(\rho)$  can arise due to its very steep variation with  $\rho$ : a 10% variation of the density changes  $T_g$  by a factor 2 [5, 7]. In this situation, slight details in the static structure might become relevant. The previous corrections for hard and soft spheres can be adapted by first noticing that the critical temperature  $T_g(\rho)$  is well estimated from the critical packing fraction of hard spheres  $\eta_g = \frac{\pi}{6}\rho d_{HS}^3(T, \rho)$  where  $d_{HS}(T, \rho)$  is a suitably defined hard-sphere diameter (see eg. [5] and [20]). In this spirit, we found (figure 2) that an even simpler formula  $\frac{\pi}{6}\rho d_{HS}^3(T) = 0.58$  fits very well the data of ref. [5] when the diameter is taken as the distance at which the reduced potential has a value  $\ln(a)$  [19]:  $d_{HS}(T) = \sigma[\frac{2}{1+\sqrt{aT^*}}]^{1/6}$ , with  $a = 0.8$ .  $T_g^{MCT}(\rho)$  is also well fitted by a similar law with  $a = 0.5$  for the effective diameter  $d_{eff}(T)$ . Considering this as a seed, we computed the structure with an effective packing fraction  $\eta^{eff} = \eta - \Delta\eta$  with  $\Delta\eta = 0.58(1/d_{HS}^3(T) - 1/d_{eff}^3(T))$ .

The results is shown in figure 2. With the proposed modification,  $\tilde{T}_g^{MCT}(\rho)$  falls nearly exactly on the fitted law. As a check of the sensitivity to the choice of  $\Delta\eta$ , the equation was solved by fixing it to the value for  $T_g^{MCT}(\rho)$  (ie the critical temperature predicted from the original MCT, for each density  $\rho$ ). The results shown by triangles are close to the simulation of [18] which differ slightly from those of refs [5] (this difference is clearly visible on the enlarged scale used in figure 2). This might reflect different characterization of the glass (see e.g. [21]). The closeness of the triangles with the simulations of [18] is probably fortuitous, and there is a priori no reason to keep  $\Delta\eta$  fixed. With the definition of  $\eta^{eff}$  indicated above ( hence with a temperature dependent  $\Delta\eta$  ), we considered a standard LJ mixture at the state point studied in [7]: one finds  $T_g^{MCT} = 0.922$  more than twice the simulation value  $T_g^{ex} = 0.435$ . With the modified MCT, we get  $\tilde{T}_g^{MCT} = 0.56$ , again definitively better than the original one (to speed the calculations, the static structure was computed from the closure of ref. [22]).

Encouraged by these results, we finally considered the square well potential with short interaction range, a prototype for colloidal glasses for which an additional mechanism of dynamical arrest - the attractive glass - has been evidenced [3]. In this case, the MCT glass lines can be superimposed to simulation only with the help of a double linear

transformation of both temperature and density [6]. In figure 3, we show the result from the modified MCT equation using a temperature independent correction  $\Delta\eta$ , a temperature dependent one  $\Delta\eta(T)$  with a linear dependence on  $1/T^*$  adjusted from a single simulation point besides the HS value, and lastly both  $\Delta\eta(T)$  and an effective temperature  $T_{eff}^* = T^* + 0.18$  ( to prevent cristallization, the simulation are actually for a slightly asymmetric mixture while we solved the MCT for the one-component fluid in order to compare with ref. [3]). Even in this more complex situation in which the mechanism for the arrest involves the formation of long-lived bonds, this way of reducing correlations leads to a clear improvement over the original MCT predictions.

In conclusion, independently of the correctness of the view that attributes the quantitative insufficiency of MCT to the factorization approximation, there is little doubt that the method proposed here for tempering correlations definitely improves the accuracy of the present form of MCT, insofar as the long time results are concerned. Besides the operational value of this modification for accurately predicting the ideal glass transition for quite disparate potential, it is expected that these results that emphasize again the importance of many-body correlations and the presence of general mechanisms common to a wide class of models will stimulate studies from first principles. In the framework of microscopic theories, the extension of this idea to the time dependent quantities, by taking account different time scales, is for example conceivable. This should go in parallel with the development of more global approaches. Finally, this significant improvement of the MCT predictions that are relative to an idealized description of the glass transition should be useful in a step by step progress towards a better understanding of the complex phenomena that occur in real glass forming liquids.

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## Figures

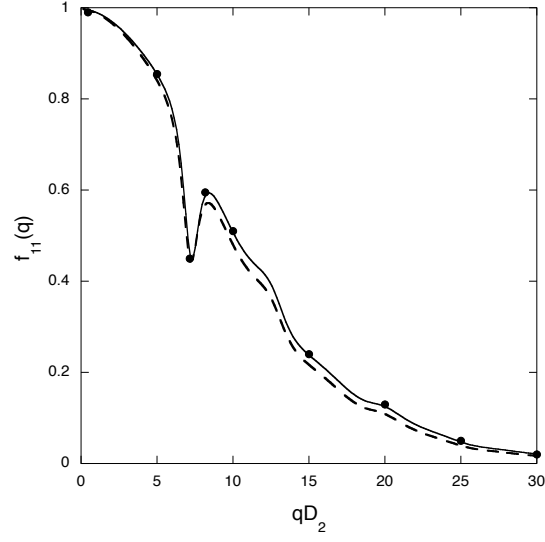


Figure 1: Non-ergodicity parameter  $f_{11}(q)$  in a binary hard-sphere mixture with  $D_1/D_2 = 0.6$  and  $\hat{x} = 0.2$  at the glass transition, Solid line: modified MCT ( $\tilde{\eta}_g^{MCT} = 0.593$ ); dashes: original MCT [12] ( $\eta_g^{MCT} = 0.5275$ ); Symbols: simulation [15] ( $\eta_g^{ex} = 0.606$ ).

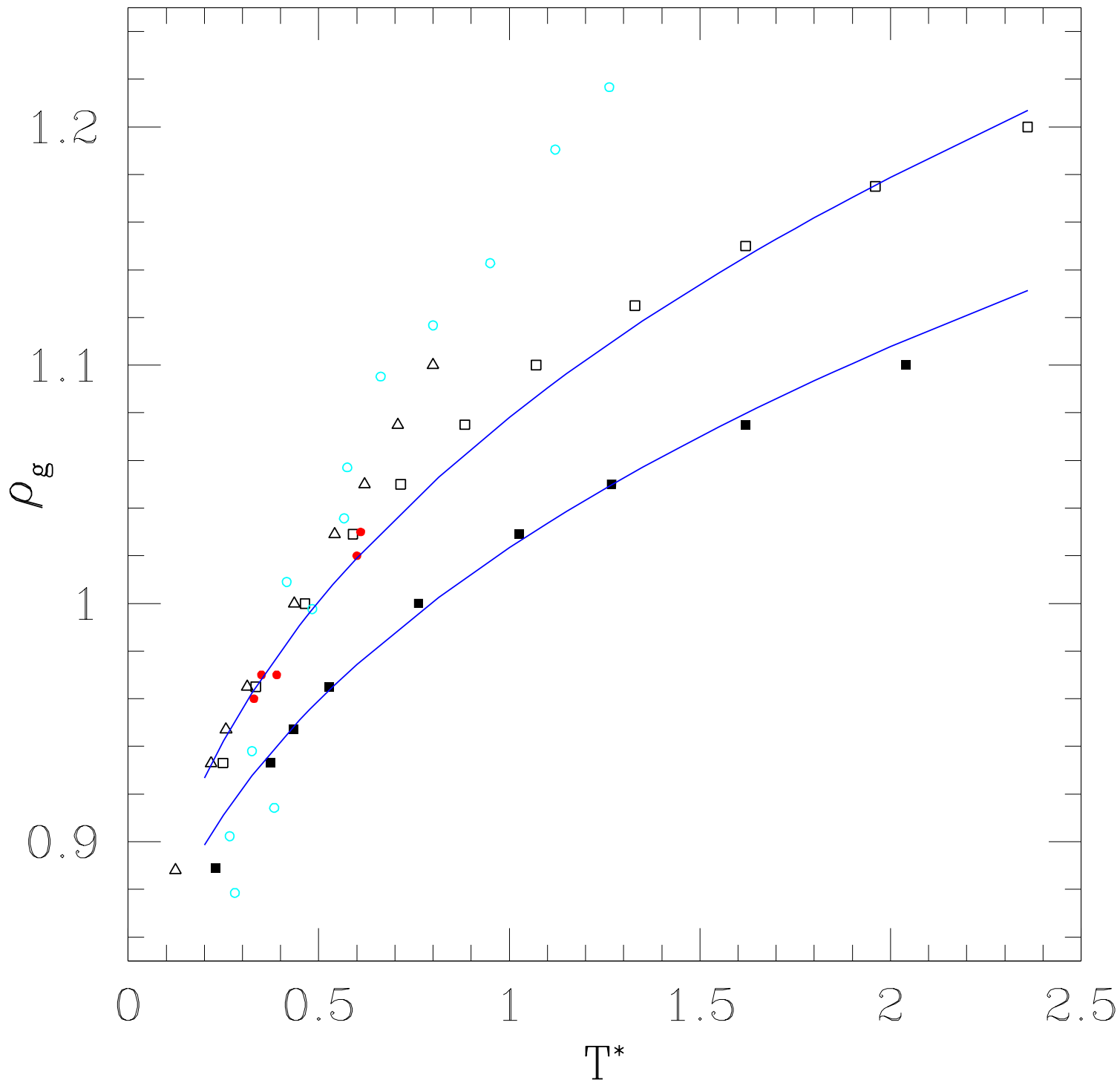


Figure 2: Glass transition line for the Lennard-Jones fluid.

Filled squares and curve: original MCT and fitted curve with  $a = 0.5$  in the effective diameter; Empty squares: modified MCT and curve adjusted to the simulation of [5] (filled circles) with  $a = 0.8$ ; triangles: Modified MCT with fixed  $\Delta\eta$ ; empty circle: simulations of [18]



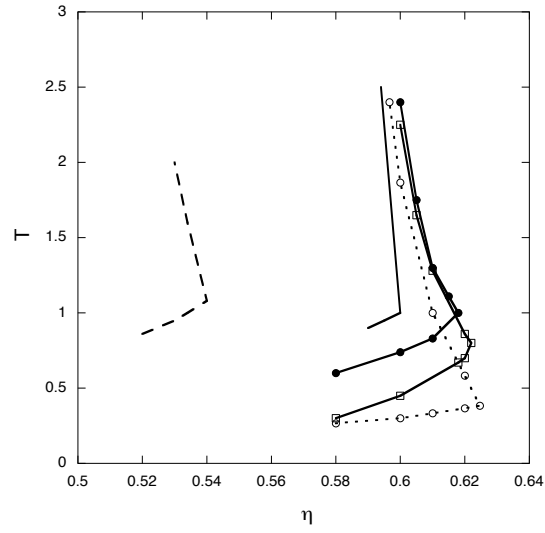


Figure 3: predicted glass transition lines for the square well fluid.  
Dashes: original MCT; solid line without symbols: modified MCT with  $\Delta\eta = 0.055$ ;  
filled circles:  $\Delta\eta(T)$ ; squares :  $\Delta\eta(T)$  and  $T^{eff}$ . The theoretical results are for the  
one-component fluid with width  $0.031\sigma$ . The dotted curve with empty circles shows the  
simulation data extracted from ref. [6].